

## Description

### White Solid Photoinitiator in the Form of Powder and Preparation Thereof

#### Technical field

- [0001] This invention is related to a white solid photoinitiator in the form of powder consisting of 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one (COMPOUND1) and to the procedure for its preparation.
- [0002] COMPOUND1 obtained through the procedure of the invention is particularly reactive as photoinitiator in photopolymerizable systems and it is easily and completely soluble in such systems in the quantities useful for the photopolymerization.

#### Background Art

- [0003] The known photopolymerizable systems contain a photoinitiator possessing in the molecule a functional group that, by electromagnetic excitation, generally UV radiation, produces radicals able to polymerize the system.
- [0004] In EP 3002 A numerous alpha-hydroxyketons are described together with their uses as photoinitiators; particularly in Example 5 the use as photoinitiator of 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one (compound No. 21), obtained in form of wax and with boiling point of 220° C at 0.05 mmHg, is described .

#### Disclosure of Invention

- [0005] We have now found that 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one obtained as a white solid in the form of powder is easy to handle and completely soluble in the quantities useful for the photopolymerization in the photopolymerizable systems that contain it as photoinitiator.
- [0006] It is therefore a fundamental object of the present invention the white solid photoinitiator, in the form of powder, consisting of 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one (COMPOUND1) and having melting point between 96° and 99°C, product not previously described in the literature.
- [0007] The product of the invention is particularly interesting when used as photoinitiator in formulations either of the transparent or pigmented kind,

since it allows to obtain very good photocrosslinking rates, notably higher than those of analogous products normally used and commercially available; moreover it provides good colour stability to photopolymerized transparent systems.

- [0008] Such characteristics render the product of the invention particularly innovative and desirable for industrial use because of the high line speed that it allows to practise.
- [0009] It is a further object of the present invention the procedure for the preparation of 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one as white solid in the form of powder (COMPOUND1) including the following steps:
  - [0010] a) Friedel Crafts reaction of diphenylether with an acylating agent selected between alpha-bromoisobutyryl bromide and alpha-chloroisobutyryl chloride, catalyzed by Lewis acids;
  - [0011] b) reaction of 2-bromo-1-{4-[4-(2-bromo-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one (or of 2-chloro-1-{4-[4-(2-chloro-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one) obtained in step a) with hydrated bases, at a temperature comprised between 10°C and 50°C, preferably between 15°C and 40°C, to give 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one dissolved in solvent;
  - [0012] c) crystallization of the thus obtained product.
- [0013] The Friedel Crafts reaction of step a) is performed preparing a solution of acylating agent and diphenylether, in a molar ratio comprised between 2.0 and 2.2, in dichloromethane or other solvent, as, by way of example, chlorobenzene, and then adding the Lewis acid, preferably AlCl<sub>3</sub>, in portions to the solution, maintaining the temperature between -20°C and 20°C, preferably between -5°C and 5°C.
- [0014] The Friedel Crafts reaction of step a) normally includes a final quenching phase, wherein the reaction mixture is poured in diluted acidic water solution, the separation of phases and the washings of the organic phase (where the reaction product is dissolved) with water or brine; such organic phase can be used as such in step b), or after evaporation of the solvent.

- [0015] The reaction mixture of step b) can be indifferently monophasic or biphasic according to the solvent used; whenever the reaction mixture is biphasic, it is preferable to add a phase transfer catalyst such as benzyltriethylammonium chloride (BTEAC).
- [0016] In the preferred forms of realization of the invention, the solvent of step a) is evaporated before proceeding with step b) and the product of reaction of step a) is dissolved in an aliphatic alcohol miscible with water, particularly in isopropanol.
- [0017] The hydrated base commonly used in step b) is selected among NaOH, KOH or Ba(OH)<sub>2</sub> in aqueous solution at 20-50 % w/w; preferably the hydrated base is NaOH.
- [0018] According to a fundamental aspect of the procedure according to the invention, COMPOUND1 is directly obtained by crystallization from the reaction mixture.
- [0019] The crystallization takes place from the solvent in which 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one is dissolved after step b), through partial distillation of the solvent and cooling or through partial evaporation of the solvent and dilution with lipophilic solvents, such as petroleum ether or hexane.
- [0020] COMPOUND1 can be also obtained by precipitation, filtration and drying, by adding to the residue obtained after evaporation of the solvent at the end of step b) one or more solvents selected among: ethyl acetate and toluene, both as such or in mixture with petroleum ether; isopropanol, n-propanol, ethyl alcohol or mixtures thereof, optionally in mixture with water; n-butyl alcohol; isobutyl alcohol; t-butyl alcohol.
- [0021] In the preferred forms of realization of the invention, when the reaction of step b) is performed in an alcohol miscible with water, such as isopropanol, 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one is obtained as a white solid in the form of powder with a melting point between 96 and 99°C (COMPOUND1) by the following phases: addition of from 0.5 to 2.0 parts by weight of water for every part by weight of isopropanol at the end of the reaction of step b); cooling at a temperature between 0°C and 10 °C; collecting by filtration the

thus obtained precipitate; drying at a temperature comprised between 20°C and 60°C.

- [0022] COMPOUND1 according to the invention is a white solid photoinitiator in the form of powder having a melting point between 96° and 99°C, it is easily soluble in the photopolymerizable systems in the quantities normally used for photopolymerization, and it mainly consists of the para-para isomer, 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one; 300 MHz <sup>1</sup>H-NMR do not indicate the presence of the other isomers.
- [0023] In the present text, with the expression "photopolymerizable system" or "photopolymerizable formulation", we mean a mixture of reactive monomers and/or oligomers, at least a photoinitiator, fillers, dispersants and other additives of general use.
- [0024] The term "photopolymerization" has a broad meaning and comprises, for example, the further polymerization or crosslinking of polymeric material, for example pre-polymers, the homo-polymerization and the copolymerization of simple monomers and the combination of these types of reactions.
- [0025] Useful monomers for photopolymerizable systems include, for example: acrylonitrile, acrylamide and derivatives thereof, vinyl ethers, N-vinylpirrolidone, mono and polyfunctional allyl ethers such as trimethylopropanediallyl ether, styrene and alpha-methylstyrene, esters of acrylic and methacrylic acid with aliphatic alcohols, with glycols, with polyhydroxylates compounds such as pentaerythritol and trimethylopropane or with aminoalcohols, esters of vinyl alcohol with aliphatic or acrylic acids, derivatives of fumaric and maleic acid.
- [0026] Useful oligomers for photopolymerizable systems are for example: polyesters, polyacrylates, polyurethanes, epoxidic resins, polyethers with acrylic, maleic or fumaric functionality.
- [0027] COMPOUND1 of the invention acts as photoinitiator and can be used alone or in combination with other photoinitiators such as for example benzophenone and its derivatives (such as methylbenzophenone, trimethylbenzophenone), acetophenone and its derivatives, for example alpha-hydroxyacetophenones, alpha-aminoacetophenones, di-

alkoxyacetophenones, (such as oligo - [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]-propanone], 2-hydroxy-2-methyl-1-phenyl-propanone, alpha-hydroxycyclohexyl phenyl ketone, 2-hydroxy-1-[4-(2-hydroxy-ethoxy)-phenyl]-2-methyl-propan-1-one, 2-dimethylamino-2-(4-methylbenzyl)-1-(4-morfolin-4-yl-phenyl)-butan-1-one, 2-benzyl-2-dimethylamino-1-(3,4-dimetossi-phenyl)-butan-1-one, 2-benzyl-2-dimethylamino-1-(4-morfolin-4-yl-phenyl)-butan-1-one, 2-methyl-1-(4-methylsulfanyl-phenyl)-2-morfolin-4-yl-propan-1-one, 1-[2,3-dihydro-1-[4-(2-hydroxy-2-methyl-1-oxopropyl)phenyl]-1,3,3-trimethyl-1H-inden-5-yl]-2-hydroxy-2-methyl-1-propanone, 1-[2,3-dihydro-3-[4-(2-hydroxy-2-methyl-1-oxopropyl)phenyl]-1,1,3-trimethyl-1H-inden-5-yl]-2-hydroxy-2-methyl-1-propanone, 4,3'-bis(alpha,alpha-hydroxy-isobutyryl)-diphenylmethane, 4,4'-bis(alpha,alpha-hydroxy-isobutyryl)-diphenylmethane, ketosulphones (such as 1-[4-(4-benzoyl-phenylsulfanyl)-phenyl]-2-methyl-2-(toluene-4-sulfonyl)-propan-1-one), benzoin ethers, benzyl ketals (such as benzyl dimethyl ketal), phenylglyoxylate and its derivatives (such as phenylglyoxylic acid methylester, ethyl ester of 2-(2-oxo-2-phenyl-acetoxy-ethoxyethyl) oxyphenylacetic acid), monoacylphosphine oxides, such as (2,4,6-trimethylbenzoyl)-diphenyl-phosphine oxide or the ethyl ester of phenyl-(2,4,6-trimethylbenzoyl)-phosphinic acid, bisacylphosphine oxides, (such as bis-(2,6-dimethoxybenzoyl)-(2,4,4-trimethyl-pent-1-yl)phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide, bis(2,4,6-trimethylbenzoyl)-(2,4-dipentoxyphenyl)phosphine oxide), trisacylphosphine oxides, halogenomethyltriazine, ferrocene derivatives or titanocenes, photoinitiators containing the borate or O-acyloxyimic group, sulphonium, phosphonium or aromatic iodonium salts.

- [0028] The utilisation of COMPOUND1 of the invention with tertiary amines (such as the triethylamine, N-methyldiethanolamine, esters of p-dimethylamino benzoic acid), that increase the speed of crosslinking by reducing the inhibitory effect of oxygen, is particularly advantageous.
- [0029] Besides COMPOUND1 of the invention, many components can be included in the photopolymerizable systems, for example thermal stabilizers, dyes or pigments, sensitizers, photooxidation stabilizers as sterically hindered amines, antioxidants, oxygen inhibitors, thermal

radicals generators such as organic and inorganic peroxides, peresters, hydroperoxides, benzopinacols, azoderivatives such as azaisobutyronitrile, metallic compounds such as cobalt(II) salts, manganese, antifoam, fillers, glass and carbon fibres, tixotropic agents.

- [0030] Other components that can be included are non-photopolymerizable polymers present as inactive substances, as for example nitrocellulose, polyacrylic esters, polyolefines etc., or polymers that are crosslinkable with other systems (for example with peroxides, atmospheric oxygen, acid catalysts or thermal activation) such as polyisocyanates, urea, melamine or epoxidic resins.
- [0031] COMPOUND1 of the invention is generally used in the photopolymerizable system in a quantity of 0.01 to 20% by weight, preferably of 0.5 to 5% by weight, on the total weight of the photopolymerizable system, and it is highly compatible with the system, while imparting to it an increased photochemical reactivity.
- [0032] It is a further object of the present invention a method for the preparation of a photopolymerizable system through solubilization of the white solid photoinitiator in the form of powder, with a melting point between 96° and 99°C, consisting of 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one, (COMPOUND1), in a quantity of 0.01 to 20% by weight, preferably of 0.5 to 5% by weight, in one or more reactive ethylenically unsaturated monomer and/or oligomer at a temperature between 20 and 60°C.
- [0033] Examples of sources of light useful for the photopolymerization of the photopolymerizable systems prepared according to the invention are mercury vapour or superactinic or excimers lamps, with emission bands in the UV-visible region.
- [0034] Among the possible useful sources of light, sunlight and other artificial sources emitting electromagnetic radiation with a wavelenght from 180 nm up to the IR region are also included.
- [0035] COMPOUND1 according to the invention acts as an efficient photoinitiator both in transparent systems and, surprisingly, in pigmented systems, and it is for instance useful for the preparation of photocrosslinkable inks, in photopolymerizable formulations for wood coating, paper, plastics, metals,

in overprint coating systems, in printing inks, in varnishes, in powder coating, in the electronics, for instance for the production of printed circuits, in microelectronic and in general in all those applications in which it is useful the formation of radicals through electromagnetic radiation.

- [0036] It is therefore a further object of the invention a method for the coating of wooden surfaces, of paper, cardboard, plastics or metal through the application of a photo-crosslinkable system prepared by dissolution of the white solid photoinitiator in the form of powder having a melting point between 96° and 99°C and consisting of 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one, (COMPOUND1), in one or more reactive ethylenically unsaturated monomers and/or oligomers and the subsequent photopolymerization with a source of light with emission bands in the UV-visible range.

- [0037] Example 1

- [0038] Preparation of COMPOUND1.

- [0039] I. Synthesis of 2-bromo-1-[4-[4-(2-bromo-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one.

- [0040] To a solution of 5 g (29.37 mmols) of diphenylether and 15.23 g (64.61 mmols) of alpha-bromoisobutirylbromide (purity 97.5 % by weight) in 50 ml of dichloromethane in about 30' 8.61 g (64.61 mmols) of aluminum trichloride were added, maintaining the temperature between 0° and 5 °C. After 1.5 h the reaction mixture was poured in a mixture of 200 ml of water and ice and 4 ml of 37% HCl. The organic phase was separated and washed with brine, dried on sodium sulphate, and filtered. A sample obtained after evaporation of the solvent was analysed.

- [0041] NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 8.25 (d, 4H); 7.1 (d, 4H); 2.07 (s, 12H).

- [0042] II. Synthesis of 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one.

- [0043] To the solution of 2-Bromo-1-[4-[4-(2-bromo-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one 13.75 g (29.37 mmol) 8.46 g (105.73 mmol) of NaOH at 50 %, 137 mg of BTEAC at 50% and 50 ml of dichloromethane were added, and the solution refluxed for 2h. After dilution with 50 ml of water and 50 ml of dichloromethane, the phases

were separated. The organic phase was washed with water and with a solution of NaCl, dried on sodium sulphate and filtered off.

- [0044] Crystallization of COMPOUND1.
- [0045] The solvent was partially evaporated from the solution obtained in II to a residual volume of 25-30 ml. By cooling, 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one was separated as a white solid, filtered and vacuum dried at 50°C; 4.9 g of powder having m.p. 96°-98 °C are obtained (COMPOUND1).
- [0046]  $^1\text{H-NMR}$  analysis at 300 MHz does not show the presence of other isomers.
- [0047] Part of the product was crystallized from toluene, obtaining a product with a melting point of 97°-99 °C.
- [0048] NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 8.10 (d, 4H); 7.07 (d, 4H); 3.9, (s, 2H); 1.63 (s, 12H).
- [0049] EXAMPLE 2.
- [0050] Preparation of COMPOUND1.
- [0051] I. Synthesis of 2-bromo-1-[4-[4-(2-bromo-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one
- [0052] The reaction was performed as described as in Example 1 (I.), starting from 45.26 g of diphenylether.
- [0053] II. Synthesis of 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one.
- [0054] From the solution obtained in I the solvent was evaporated under vacuum thus obtaining 131.25 g of an oil that spontaneously solidifies. The crude material so obtained is mixed under stirring with 250 ml of isopropyl alcohol then at room temperature 44.8 g of 50% NaOH (0.56 mol) were added. After 1h at room temperature under stirring the precipitate was filtered off and the solution acidified to pH 2-3 with 1M HCl .
- [0055] III. Cristallization of COMPOUND1.
- [0056] 350 ml of water were added to the thus obtained solution and the mixture was cooled to 0-10°C, obtaining a white precipitate that was easily filtered and dried in oven at 50°C; 82.17 g of product were obtained (COMPOUND1).
- [0057] m.p. = 97-98°C.

- [0058]  $^1\text{H-NMR}$  analysis at 300 MHz does not show the presence of other isomers.
- [0059] NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 8.10 (d, 4H); 7.07 (d, 4H); 3.9 (s, 2H); 1.63 (s, 12H).
- [0060] EXAMPLE 3
- [0061] Application Tests .
- [0062] The substances used for the preparation of the photopolymerizable systems evaluated in the following application tests are:
- [0063] Ebecryl ® 220 (hexafunctional aromatic urethane acrylate from UCB (Belgium);
- [0064] OTA 480 ® (trifunctional oligomer acrylate derived from glycerol, from UCB, Belgium);
- [0065] HDDA, (1,6-hexanedioldiacrylate from UCB, Belgium);
- [0066] TMPTA (trimethylolpropanetriacrylate);
- [0067] Ebecryl ® 600 (epoxyacrylate from UCB, Belgium);
- [0068] Ebecryl ® 810 (polyester acrylate from UCB, Belgium);
- [0069] TPGDA (tripropyleneglycoldiacrylate);
- [0070] Ebecryl ® 350 (additive from UCB, Belgium);
- [0071] Irgalite ® Blue BSNF from CIBA Specialty Chemicals;
- [0072] Verol 368 (dispersant from Lamberti SpA, Italy)
- [0073] As photoinitiator, the following compounds have been used:
- [0074] COMPOUND1 obtained as described in Example 1.
- [0075] Irgacure ® 184, alpha-hydroxyketone commercialised by Ciba Specialty Chemicals.
- [0076] Irgacure ® 907, aromatic aminoketone commercialised by CIBA Specialty Chemicals.
- [0077] Four formulations (I,II,III and IV) were prepared mixing respectively (% by weight):
- |        |     |               |       |
|--------|-----|---------------|-------|
| [0078] | I.  | Ebecryl ® 600 | 40%   |
| [0079] |     | TMPTA         | 30%   |
| [0080] |     | OTA 480       | 30%   |
| [0081] | II. | Ebecryl 220 ® | 75%   |
| [0082] |     | OTA 480 ®     | 12.5% |
| [0083] |     | HDDA          | 12.5% |

[0084]	III.	Ebecryl ® 810	80.0%
[0085]		TPGDA	20.0%
[0086]	IV.	Irgalite ® Blue BSNF	18.0%
[0087]		Ebecryl ® 600	37.3%
[0088]		Ebecryl ® 350	0.9%
[0089]		Ebecryl ® 220	10.4%
[0090]		TMPTA	31.9%
[0091]		Verol 368	1.5%

[0092] The photopolymerizable systems (Ia, Ib, IIa, IIb, IIIa, IIIb, IVa, IVb) were prepared dissolving the photoinitiators in the corresponding formulations (I, II, III and IV) at room temperature; the compositions of such systems (%w/w) are reported in Table 1.

[0093]

**Table 1**

	Photopolymerizable systems							
	Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb
Formulation	96	96	96	96	96	96	97	97
COMPOUND1	4	-	4	-	4	-	3	-
Irgacure ® 184	-	4		4	-	4	-	-
Irgacure ® 907	-	-	-	-	-	-	-	3

[0094]

[0095] The evaluation of the photopolymerizable systems was made by determining the reactivity parameters and the yellow and white indexes.

[0096] Reactivity

[0097] The photopolymerizable system is spread with a thickness of 50 microns on a varnished cardboard (3 microns only for the evaluation of the systems IVa and IVb) using a bar-coater and irradiated at a distance of 12 cm from the light source. A Fusion® photopolymerizer was used, equipped with a medium pressure mercury lamp with a power of 120W/cm.

[0098] The photopolymerization rate, measured in m/min, is the maximum possible speed at which a perfect superficial cure of the system is obtained (Tack Free). The perfect superficial cure is intended when the cured layer doesn't show to suffer damages from the "thumb twist test."

[0099] The maximum speed (in m/min) at which a damage of the photopolymerized system can't be seen after rubbing with abrasive paper was also measured (Superficial Abrasion); greater is the speed line, greater it is the efficiency of the system.

[00100] White and Yellow index

[00101] The photopolymerizable system is spread with a thickness of 50 microns on a varnished cardboard using a bar-coater mounted on an electric stretch-film and therefore is passed at a distance of 12 cm from the light source at a speed of 10 m/mins. A Fusion® photopolymerizator was used, equipped with a medium pressure mercury lamp with a power of 120W/cm.

[00102] White and yellow indexes were measured according to the ASTM standard D 1925-70. A low value of yellow and a high value of white, are index of a good stability of the colour of the formulation.

[00103] The results are reported in Table 2.

**Table 2**

	Tack Free	Superficial Abrasion	Yellow Index	White Index
Ia	48.5	35.0	10.1	56.2
Ib	22.0	15.0	10.0	56.3
IIa	58.0	45.0	10.4	55.7
IIb	28.5	18	12.8	50.8
IIIa	25.5	1.5*	10.9	53.3
IIIb	9.4	4*	10.6	55.1
IVa	21.0	-	-	-
IVb	22.0	-	-	-

[00104] \*number of passages (at 10 m/min) necessary not to have a visible damage of the photopolymerized system after rubbing with abrasive paper

[00105]

[00106] As shown from the reported data the presence of COMPOUND1 of the invention in the photopolymerizable systems results in a very good curing speed and in a good colour stability (index of yellow and white) of the obtained products.